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Knoop Hardness on the (0001) Plane of 4H and 6H Silicon Carbide (SiC) Single Crystals Fabricated by Physical Vapor Transport

by Jeffrey J. Swab, James W. McCauley, Brady Butler, Daniel Snoha, Donovan Harris, Andrew A. Wereszczak, and Mattison K. Ferber

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14. ABSTRACT

The Knoop hardness of 4H and 6H single crystals of silicon carbide (SiC) was determined at room temperature. X-ray diffraction techniques confirmed the crystal structure and orientation of each polytype verifying that both discs had the six-fold symmetry expected for a hexagonal crystal and that the c-axis was oriented approximately perpendicular to disc faces. This symmetry was confirmed by the Knoop hardness values on the (0001) plane of the 4H crystal, but the symmetry was not as apparent in the 6H crystal, which may indicate that the c-axis was not as nearly aligned to the faces of the 6H as it was in the 4H crystal. The Knoop hardness was determined at 15° increments around the c-axis using 0.98 and 2.94 N indentation loads. The average Knoop hardness on the (0001) plane at 0.98 N was approximately 30 GPa for both crystals with the average dropping to around 24 GPa for the 6H crystal and 23 GPa for the 4H when the indentation load was increased to 2.94 N. The difference between the maximum and minimum hardness values on the (0001) plane of both crystals at the 0.98 N indentation load was approximately 2 GPa but the difference was significantly less at 2.94 N.

15. SUBJECT TERMS

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1. Introduction

Silicon carbide (SiC) is an advanced ceramic that is widely used in a variety of applications such as abrasives, heat exchanger tubes, body and vehicle armor, and in numerous electronic devices. It has hundreds of polytypes that are based on the arrangement of successive layers of the SiC tetrahedra unit cell. The cubic crystal structure is commonly referred to as the β-phase, while the α-phase refers to polytypes with the hexagonal or rhombohedral crystal structure. The common polytype in the β-phase is 3C. The 4H and 6H, both of which have a hexagaonal crystal structure, and the 15R which is rhombohedral, are the most common polytypes in the α phase (*1*). As a result, the hardness of polycrystalline SiC can vary within a bulk specimen since numerous polytypes are typically present. Additionally the hardness should vary as a function of crystallographic orientation as suggested by the significant difference in anisotropic elastic constants (c_{ij}) (*2*), but hardness in the α phase should still exhibit hexagonal symmetry on the (0001) plane.

The data available on the hardness of single crystals of SiC is summarized in table 1 (*3*–*10*). Knoop hardness results from over 70 years ago by Peters and Knoop (*3*) and then Winchell (*4*) are quite different and may be due to differences in the polytype examined, the indentation load (which is not reported in either publication), or the level of impurities in the SiC*. Subsequent work by Shaffer (*6*) on 6H crystals found that the hardest direction (hardness values approaching 30 GPa) was on the (0001) face when the long-axis of the Knoop indenter was parallel to $(11\bar{2}0)$ plane. The lowest hardness of 21 GPa was observed when indents were placed parallel to the c-axis on the $(10\bar{1}0)$ face. Further research by Shaffer (*7*) showed that the β-phase was not significantly softer than the α-phase, however it did exhibit less hardness anisotropy. Sawyer et al (*9*) reported that the hardness on the (0001) plane of 6H SiC varied between approximately 23.5 to 25.7 GPa as a function of orientation and attributed this anisotropy to dislocation slip.

Rendtel, et al (*10*) conducted Vickers and Knoop hardness measurements using 0.24 and 19.6 N indentation loads. The Knoop hardness at a 0.24 N load was 22–27 GPa for the (0001) black and green crystals, but 25 GPa for both crystals when an indentation load of 19.6 N was used. The Vickers hardness for these crystals at these same loads was significantly less.

* The colors black, blue, green, and yellow observed in SiC and listed in table 1 are due to the presence of different impurities.

Table 1. Summary of single crystal SiC hardness data.

Reference	Method	Load (N)	H (GPa)	Comments
3	K	NA	21-22	Black
			21	Green
4	K	NA	28-30	Black (0001) face
			27-28	Green (0001) face
5	Double cone*	1.96	30-32	Blue & Green on (0001) face
			21-27	Blue & Green on (1010) face
			20-26	Blue & Green on (1120) face
6	K	0.98	29	(0001) para to (10$\bar{1}$0)
			30	(0001) para to (11$\bar{2}$0)
			21	(10$\bar{1}$0) para to c-axis
			28	(10$\bar{1}$0) per to c-axis
			24	(11$\bar{2}$0) para to c-axis
			28	(11$\bar{2}$0) per to c-axis
7	K	0.98	28-29	β-SiC on (100)
8	V	2.94	32.4	Si-terminated (0001) face
			34.3	C-terminated (0001) face
9	K	4.9	~23.5-25.7	6H Acheson
10	K	0.24	~22	Black (0001)
			~27	Green (0001)
			~28	Yellow, cubic
	V	0.24	~26	Black (0001)
			~26	Green (0001)
			~27	Yellow, cubic
	K	19.6	~25	Black & Green
	V	19.6	~28	Black & Green

Notes: K – Knoop indenter, V – Vickers indenter.
* The "double cone" indenter in reference 5 appears to give indentations similar to a Knoop indenter but it is stated to be "an adjustable diamond indenter with a circular edge produced by two cones with a common base and a common axis."

Recently nano-indentation testing of 4H and 6H crystals showed that the (0001) plane of 6H exhibited the highest hardness and that the 6H had a higher anisotropy ratio (basal to prismatic hardness) than 4H (1.16 to 1.05). These hardness results coupled with indentation fracture toughness results also performed lead the authors of the study to suggest that a SiC predominantly containing the 6H polymorph with a strong basal texture would be a preferred armor ceramic (*11*).

The present study examined the Knoop hardness of 4H and 6H single crystals of SiC at room temperature with indention loads of 0.98 N and 2.94 N and compared this data to a commercially-available polycrystalline SiC* material that is a candidate for armor applications.

2. Material Information

Two single crystal discs of SiC, one 4H and the other 6H, were fabricated using a physical vapor transport growth method†. The 4H disc was nominally 57 mm in diameter and 5 mm thick while the 6H was slightly smaller with a 41 mm diameter and 4 mm thickness. Optical images of both discs are shown in the top row of figure 1 while crossed polarizer images are shown in the bottom row. In both cases the view is down the c-axis on to the (0001) plane. Because SiC is optically isotropic in this direction the crossed polarizer images should be completely dark. The patterns and variations observed in these images indicate the presence of inhomogenities, low angle grain boundaries, and also the possibility that residual stresses are present. The many color variations in the 4H crystal probably indicate that numerous impurities are present in this crystal.

* SiC-N, CoorsTek Vista Operations, Vista, CA.
† Fairfield Crystal Technology in New Milford, CT.

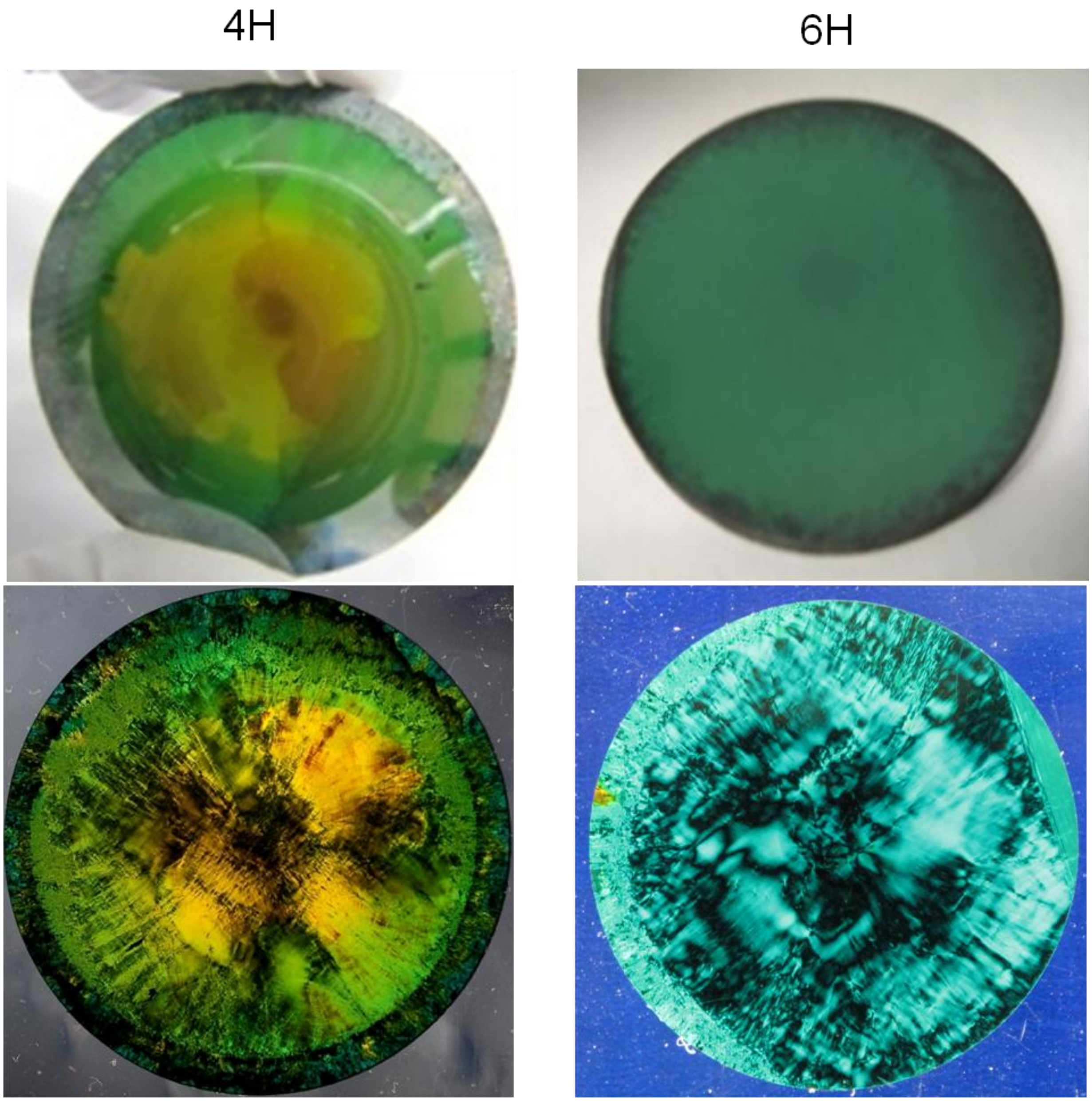

Figure 1. Optical and crossed polarizers images of the 4H and 6H SiC crystals. The top images are the optical images while the bottom images are from cross polarizers lighting.

3. Experimental Procedure

Crystallographic Orientation: the polymorphs of each disc were confirmed using X-ray diffraction with φ = 0-360°, ψ = 0-87° in 0.5° and 3° increments respectively. The 2θ value was fixed for the crystal plane of interest. The orientation was identified by analyzing orientations where this specific Bragg condition was satisfied. This analysis technique indicated

the presence of a specific polymorph, but it did not eliminate the possibility of multiple polymorphs being present within each disc.

Knoop Hardness: the procedures outlined in ASTM C1326* were followed to determine the Knoop hardness at 100 g (0.98 N) and 300 g (2.94 N). Five indentations were made at each load every 15° radially around the c-axis with the long-axis of the Knoop indent aligned along the diameter of the disc, as illustrated in figure 2. Optical and electron microscopy were used to examine the resulting indentations.

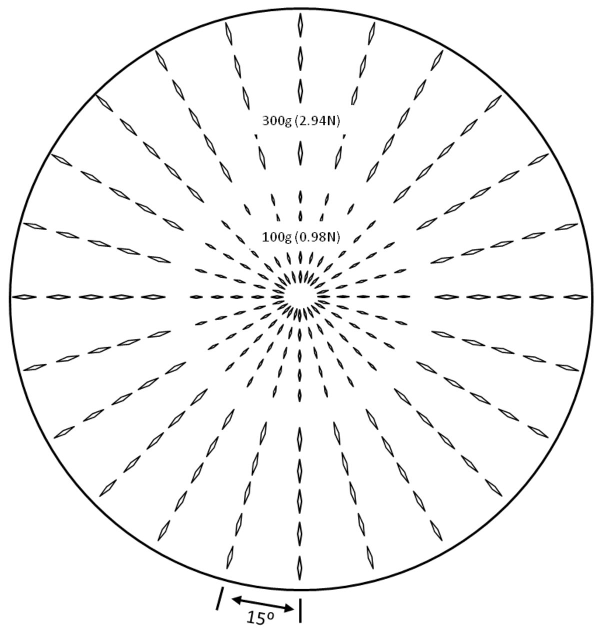

Figure 2. Schematic of the location of the Knoop indentation placement in the SiC crystals.

4. Results and Discussion

X-ray results of the 4H crystal showed six 4H (102) peaks at $2\theta = 38.235°$ and $\psi = 63°$ indicating the c-axis is approximately normal to the flat surfaces of the disc and the a-axis is 4.5° clockwise from the reference marker. Peaks measured at 57.402° confirmed that 4H (105) planes were present at $\psi = 36°$ as expected for this polytype; however, measurements taken at $2\theta = 90.250°$ showed the presence of planes that would correspond to either the 6H or 3C polytypes as well. A full set of peaks at $2\theta = 38.235°$ and $2\theta = 90.250°$ confirmed that the second disc was comprised of the 6H polymorph with the c-axis approximately normal to the flat of the disc and the a-axis 37.5° clockwise from the reference mark. A conventional 2θ scan revealed

*ASTM C1326. Standard Test Method for Determining the Knoop Hardness of Advanced Ceramics. ASTM Vol. 15.01.

faint traces of the forbidden reflections corresponding to planes normal to the c-axis and provided further confirmation that the 4H and 6H polytypes were indeed present in each respective sample.

The Knoop hardness results for each crystal (figure 3) confirms the X-ray data and shows that the 4H crystal is more symmetric, with close to six-fold symmetry, since the HK values are more consistent and repetitive around the c-axis at both indentation loads when compared to the 6H crystal. Both crystals had maximum and minimum Knoop hardness value around 31 and 29 GPa respectively at 0.98 N. At the higher indentation load this difference was much less for both crystals, around 0.5 GPa for the 4H and just less than 1 GPa for the 6H poltype. These hardness variations as a function of orientation may be the result of the significant difference in the anisotropic elastic constants previously reported (*2*). The average hardness of both crystals at 0.98 N is approximately 30 GPa (30.0 GPa for the 4H and 30.3 GPa for the 6H), but at 2.94 N the 6H is slightly harder, 24.2 GPa compared to 23.1 GPa[*]. Both polytypes are about 10% harder than the polycrystalline SiC at 0.98 N but there is essentially no difference in hardness at 2.94 N.

Representative examples of the Knoop indentations in both crystals are shown in figures 4 and 5. In general the 0.98 N indents were clean with little if any cracking occurring at tips of the indents. Lateral cracks were observed in a few instances on the 4H crystal at 0.98 N (see figure 4). At 2.94 N very short cracks (a few micrometers in length) propagated from one or both tips of the indent in both crystals.

[*]The ≈ 20 GPa Knoop hardness of the 6H crystal observed at 175° and shown in figure 2 was not included when the hardness difference and average hardness values were calculated.

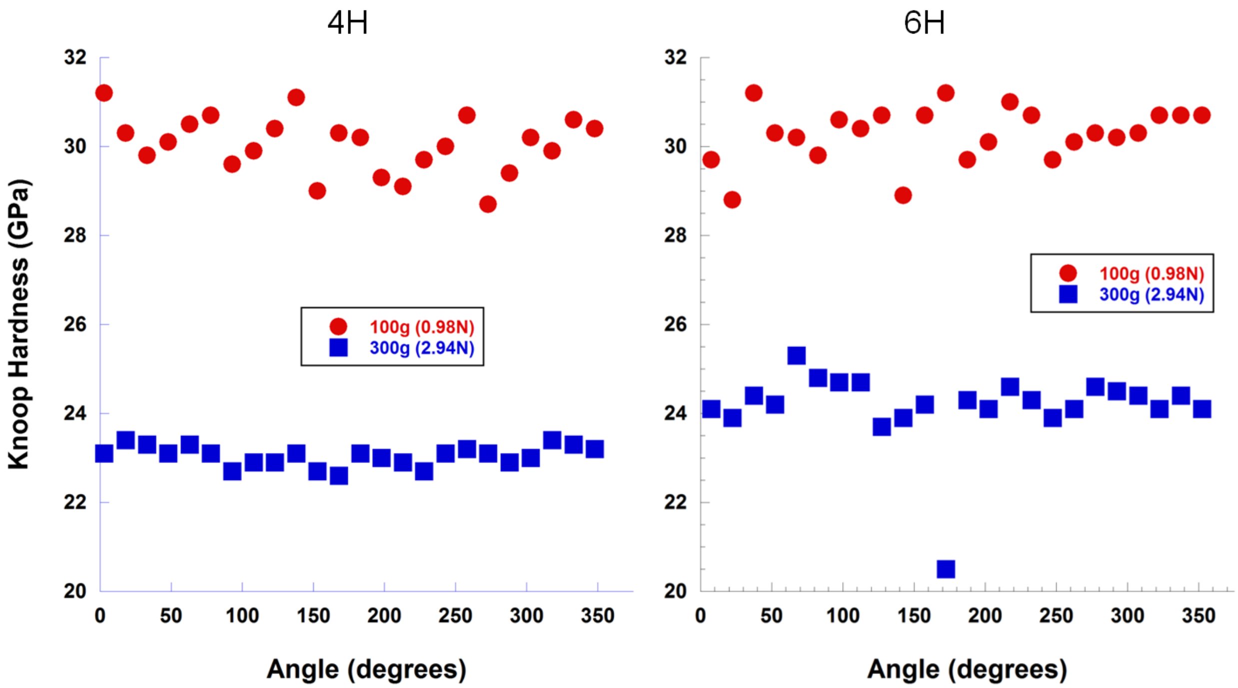

Figure 3. Plot of Knoop hardness as a function of the radial angle around the c-axis. Left plot is the 4H and the right the 6H.

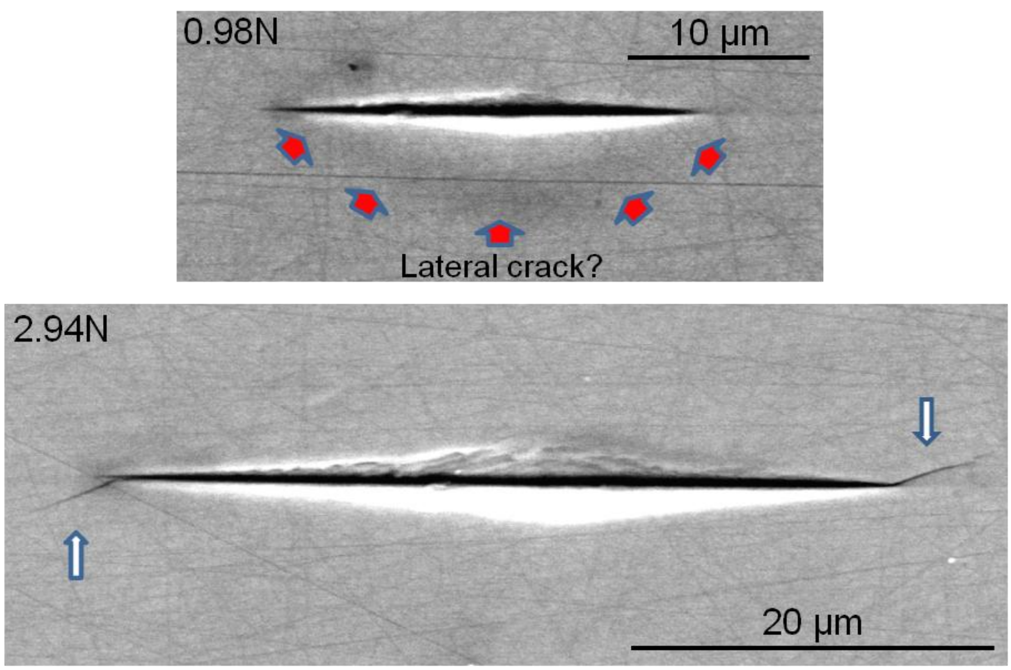

Figure 4. Images of the Knoop indents in the 4H SiC crystal using indentation loads of 0.98 N (top) and 2.94 N (bottom). The arrows highlight some of the minor cracking associated with these indentations. Red arrows highlight a possible lateral crack associated with a 0.98 N indent. White arrows show the short radial cracks that can come off the tips of the 2.94 N indents.

Since the 4H disc was more symmetric about the c-axis and larger in size additional Knoop hardness measurements were made at 0.49, 7.85 and 19.61 N. Table 2 summarizes the average Knoop hardness values for over 100 indents made at each indentation load. There is a pronounced decrease in the Knoop hardness of the 4H crystal with increasing load indicative of the well documented indentation size effect that has been observed in numerous polycrystalline and single crystal ceramic materials (*12–15*).

Table 2. Knoop hardness data for 4H and 6H SiC single crystals and SiC-N.

	4H		6H		SiC-N	
Load (N)	**Ave HK (GPa)**	**STDEV**	**Ave HK (GPa)**	**STDEV**	**Ave HK (GPa)**	**STDEV**
0.49	39.5	2.2	NA	NA	NA	NA
0.98	30	1.0	30.3	1.2	26.2	1.0
2.94	23.1	0.5	24.2	1.1	24.2	1.3
7.85	22.4	0.9	NA	NA	NA	NA
19.61	19.5	0.7	NA	NA	20.5	0.2

The Knoop hardness values at the 0.98 N indentation load are in excellent agreement with the earlier values given by Shaffer (*6*) for the (0001) plane. However, the value generated by Rendtlel, et al. (*9*) at 19.6 N is approximately 20% higher and their values at 0.24 N do not fit the hardness-load trend for the 4H crystal shown in table 2. The study showed that the Knoop hardness for single crystals as well as several polycrystalline SiC materials increased when the indentation load was increased from 0.24 to 0.48 N, then the hardness gradually dropped as the load was increased beyond 0.48 N. These discrepancies may be due to differences in the polytypes examined and/or impurity levels in the crystals.

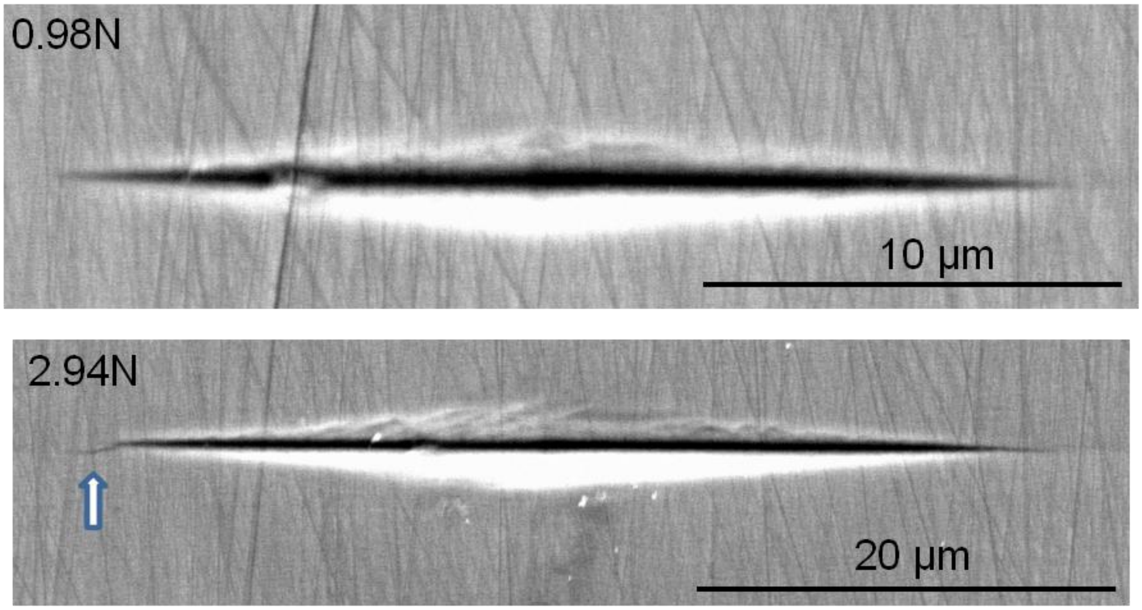

Figure 5. Images of the Knoop indents in the 6H SiC crystal using indentation loads of 0.98 N (top) and 2.94 N (bottom). White arrows show the short radial cracks that can come off the tips of the 2.94 N indents.

In an attempt to alternatively observe differences in each materials response to the indentation process, spherical indentations were done up to maximum loads of 20 and 100 N using a diamond indenter with a 220 µm diameter. The indentation testing was done using a microhardness tester (Model Z2.5, Zwick USA, Kennesaw, GA) equipped with an indenter-depth-of-penetration sensor. Indentation was done in displacement control at a rate of 1 µm/s for both loading and unloading. Figure 6 is the load-displacement plot at 20 N that shows nothing unusual in any of the loading/unloading curves (e.g., rapid drops in force due to sudden compliance increases or damage introductions into the material) and that all three materials exhibit very similar behaviors. All three materials also exhibited a similar behavior when the indentation load was increased to 100 N.

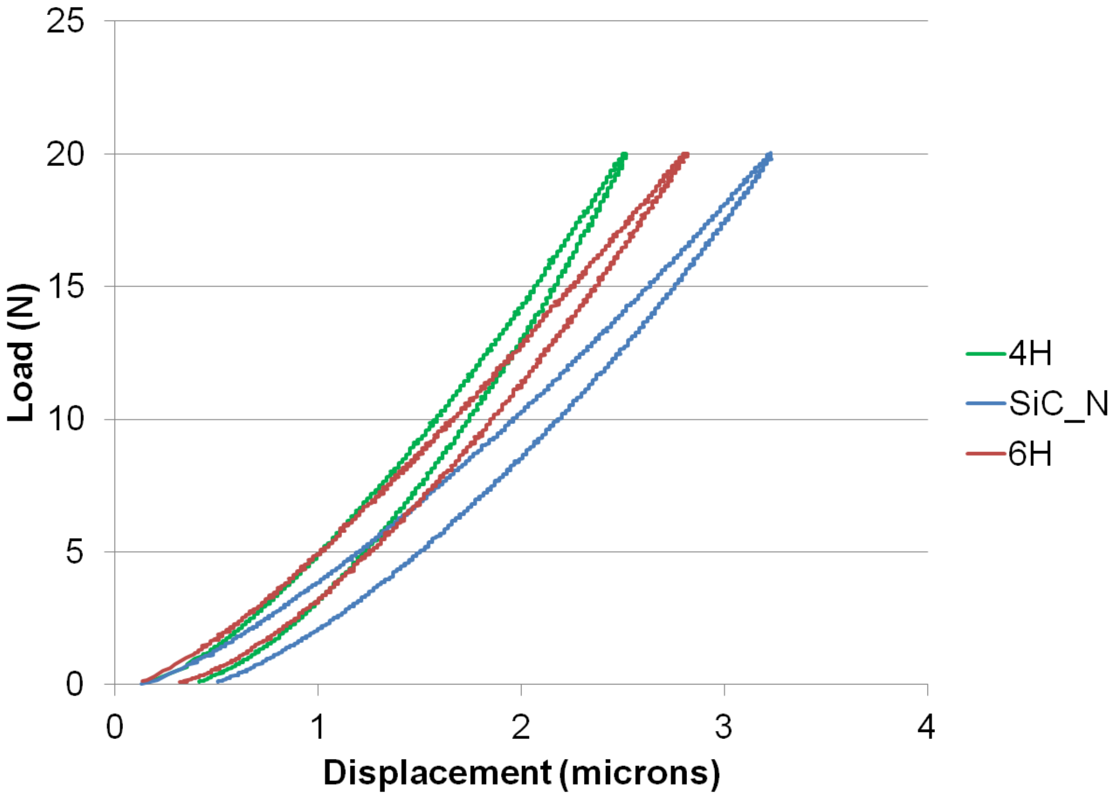

Figure 6. Load-Displacement curves from spherical indentation tests conducted at 20 N.

5. Summary

The Knoop hardness on the (0001) plane of 4H and 6H single crystals of SiC at 0.98 and 2.94 N indentation loads was determined. The hardness variations as a function of the radial angle about the c-axis confirmed the symmetry of each crystal obtained from X-ray diffraction analysis. Based on the hardness values the symmetry of the 4H crystal was closer to the expected six-fold symmetry than the 6H crystal. Both crystals had an average hardness of approximately 30 GPa at a load of 0.98 N. This is about 12% harder than the polycrystalline SiC. However these averages dropped to 23.1 GPa for the 4H and 24.2 GPa for the 6H when the load was increased to 2.94 N. At the higher load the average hardness is essentially no different than the polycrystalline SiC at the same load. The maximum and minimum Knoop hardness values for both crystals were approximately 31 and 29 GPa respectively at the 0.98 N indentation load while at 2.94 N this difference was significantly less. Further hardness testing on the 4H showed a pronounced decrease in hardness with increasing indentation load indicative of the indentation size effect. Subsequent spherical indentation testing of both crystals as well as the polycrystalline SiC showed a similar material response in all three materials. It does not appear from these results that a SiC composed solely of the 6H or 4H polytype would be preferable as SiC armor ceramic.

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